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Zinc alloy and process for hot-dip galvannealing of steel

The present invention relates to a hot-dip coating alloy composition suitable for galvannealing steel sheet.

Galvannealed coated products are well known to the automotive industry as product with excellent properties. Weldability and paint adhesion are particularly good. Nevertheless, market needs require most coating lines to produce galvanised and galvannealed products alternatively.

During continuous hot-dip galvanising of steel sheet, a bath of molten zinc is employed. Prior to entering the bath, the sheet typically undergoes a preparatory heat treatment in a furnace with a reducing atmosphere. A so-called snout makes the connection between this preparatory furnace and the coating bath. After passing through the bath, the desired coating thickness is obtained by means of air knives.

When galvannealing is contemplated, the steel sheet undergoes an additional heat treatment in an annealing furnace so as to perform the diffusion of Fe into the Zn coating. This heat treatment is applied immediately after the hot-dip step and the operation of the air knives.

For the manufacture of galvanised as well as galvannealed products, at least some Al is typically added to the molten zinc bath for controlling Fe-Zn alloy growth during the passage of the steel sheet through the bath.

For the production of galvanised steel, a relatively high Al concentration of more than 0.13 wt.% is normally used. The main advantage of a high concentration of Al is that the formation of intermetallic Fe-Zn compounds in the bulk of the bath is

avoided. These compounds, called bottom dross, have a tendency to slowly sink to the bottom of the bath. They also tend to form a deposit on the surface of the galvanised products, thereby jeopardising their surface quality. The high Al concentration results in the formation of some Fe-Zn-Al intermetallic compounds, called top dross, because of their tendency to float on the bath surface. This type of dross is however easy to deal with as it can readily be skimmed off from the surface. This high Al bath moreover produces a dense and impermeable $Fe_2Al_5Zn_x$ inhibition layer on the steel/zinc interface.

For the production of galvannealed steel however, hot-dipping in the Zn alloy bath should result in the formation of a relatively permeable $Fe_2Al_5Zn_x$ inhibition layer on the steel/zinc interface. Indeed, the object of the subsequent annealing step is precisely the formation of a Fe-Zn alloy, a process whereby Fe has to migrate freely through the steel/zinc interface. The permeability of the interface is normally achieved by using a Zn alloy bath with a relatively low Al content of less than 0.13 wt.%.

The compromise sought between the danger of formation of bottom dross at too low Al contents, and the formation of an impermeable $Fe_2Al_5Zn_x$ layer at too high Al contents, renders the optimal Al concentration extremely critical. Moreover, the optimal amount of Al is still too low to avoid bottom dross formation and the resulting significant loss of Zn. Further problems linked to the low Al concentration are:

- accelerated corrosion of the immersed equipment;
- bottom dross entrapment on the steel sheet;
- deposition of intermetallic compounds on the immersed equipment, in particular on the rolls.

The Al concentration problem is further exacerbated when a manufacturer needs to switch between galvanising and galvannealing. Conventionally, two methods are used to cope with the need to change the Al content of the bath when switching between both processes.

A first method is to provide two different baths. The drawbacks of this approach are the higher equipment cost and the reduced flexibility of the line.

A second method is to use a single bath and to significantly change its Al content according to the particular process applied. However, the elevation of the Al concentration when switching from galvannealing to galvanising results in the conversion of bottom dross into floating dross. Floating dross particles are picked-up by the rolls in the bath and transferred to the surface of the sheet, producing pimples and print-through defects. Main drawbacks of this procedure are the unavoidable concentration gradients in the bath, and the impossibility to maintain a high coating quality during process changes.

WO0031311 describes a process whereby the same Al level of 0.10 to 0.15 wt.% is used when galvanising and galvannealing. This Al-level must further be combined with a lower than typical bath temperature of 445 °C and with continuous bath mixing. The decreased bath temperature, which is needed to decrease the iron solubility, is doubtfully feasible on a real production line. Also, the use of extra circulation in the bath may enhance the dross pick-up by the rolls.

Other patents or patent applications like WO01/55468, EP1070765 and JP03-166352 focus more on the mechanical design of the galvanising bath and on methods to remove the dross in order to solve the dross-related problems.

Some authors describe possibilities to increase the alloying kinetics, especially by modifying the steel surface in order to enhance the Fe-Zn reaction after the breakdown of the $Fe_2Al_5Zn_x$ intermetallic layer. JP08-291379 and JP04-254530 describe the use of the so-called pre-oxidation and subsequent reduction, during which a reactive metallic surface layer is created.

It is an object of this invention to provide for a Zn alloy bath especially designed to overcome the above mentioned problems.

According to the invention, a Zn-alloy is provided for hot-dip galvannealing steel, characterised in that it contains 0.12 to 0.35 wt.% Al and 0.02 to 0.11 wt.% Cr. Preferably, the alloy contains 0.135 to 0.29 wt.% Al and 0.05 to 0.10 wt.% Cr. As a further preferred embodiment, the alloy only contains Zn and unavoidable impurities.

The invention also encompasses a process for coating steel on an individual hot-dip line, comprising, in either order, the steps of:

- galvanising a first quantity of steel by hot-dipping in a Zn alloy bath;
- galvannealing a second quantity of steel by hot-dipping in the Zn alloy bath and by subjecting the coated steel hereby produced to a thermal treatment in an annealing furnace,

characterised in that the Zn alloy contains Al and 0.05 to 0.10 wt.% Cr.

A further embodiment concerns a process for galvannealing dual-phase steel by hot-dipping in a Zn alloy bath, characterised in that the Zn alloy contains 0.12 to 0.35 wt.% Al and 0.02 to 0.11 wt.% Cr

The invention also realises a lowering the specific energy consumption of a furnace used for annealing a product after hot-dipping in a Zn alloy bath, by performing either one or both steps of:

- lowering the maximal surface temperature reached by the hot-dipped product in the annealing furnace; or,

- lowering the residence time of the hot-dipped product in the annealing furnace;

whereby at least 0.02 % Cr is added to the Zn alloy bath.

It should be noted that the mentioned concentrations correspond to the bulk analysis of the bath, i.e. including undissolved floating compounds.

It has indeed been found that the addition of 0.02 to 0.11 wt.% Cr accelerates the Fe migration kinetics during the galvannealing treatment by weakening the inhibition layer present at the steel/zinc interface.

This effect can be exploited in several ways.

The enhanced Fe migration through the inhibition layer allows for an increase in the Al content of the alloy used for galvannealing. This effect is particularly useful for galvannealing high-strength Si and P rich steels, which, as a rule, show low Fe diffusivity into the coating during annealing. Indeed, for such steels, very low Al amounts, down to 0.10 wt.%, are classically called for. A considerable quantity of bottom dross is unavoidable in these conditions. According to the present invention, the Al content can be raised to 0.12 wt.% or event to 0.135 wt.% or more. The formation of bottom dross is thus considerably reduced.

Another related effect occurs when processing classical steel types, in particular when the line is switched from galvannealing to galvanisation. By using aforementioned amount of Cr during galvannealing, the Al content of the bath can be subtantially increased. The formation of bottom dross is therefore totally avoided at this stage. Switching to galvanisation therefore does not result in the production of floating dross, even if the Al content of the bath is hereby increased.

Consequently, the critical compromise between the production of bottom dross and insufficient Fe migration, is considerably eased. The higher allowable Al concentration permits manufacturers to maintain a relatively high Al concentration in their bath when switching form galvanising to galvannealing. Although some top dross may be formed, the formation of bottom dross, which is as explained above a serious inconvenient, is considerably reduced or even totally avoided.

The enhanced Fe migration through the inhibition layer allows for a decrease in the annealing temperature. This possibility is particularly useful for heath sensitive steels such as dual-phase steels. Indeed, such steels rapidly lose their useful properties when subject to high temperatures. With dual-phase steels are meant steels containing e.g. 0.35 Cr, 0.15 Si, 0.20 Mo; X: 0.70 Cr, 0.40 Si, 0.20 Mo.

The enhanced Fe migration through the inhibition layer allows for a decrease in the annealing time. For the production of galvannealed steel sheet, a specific energy input is needed during the annealing step to obtain the desired Fe-Zn alloying degree. In an existing installation, the annealing furnace may have become the limiting factor. The invention then permits to increase the line throughput.

Of course, the above advantages can be combined, e.g. by decreasing the residence time in the annealing furnace and by lowering the annealing temperature.

It should also be noted that Cr is an ecologically acceptable element, in particular when present in its elemental form such as in an alloy.

The reasons for maintaining an Al level of at least 0.12 wt.% are explained above. An Al level of more than 0.35 wt.% is undesirable, as the solubility, and hence the activity of Cr, decreases sharply at higher Al contents. Indeed, a minimum of 0.02 wt.% of preferably soluble Cr is needed to render the intermetallic crystals formed at the interface between the steel sheet and the zinc overlay sufficiently permeable to Fe diffusion. Given the requirement for at least 0.12 wt.% Al, it appears detrimental to add more than 0.11 wt.% Cr, as higher levels could generate process or product problems due to the presence of undissolved Cr.

The amount of Fe diffused into the coating is a measure for the annealing reactivity. Typical values are in the range between 9 and 11 % of Fe, corresponding to an Fe content in the coating of 4.5 to 5.5 g/m² for an assumed coating thickness of 7 µm.

As a first example, annealing reactivity data is produced for a typical cold-rolled multi-phase steel with, in wt.%, 0.12 C, 0.12 Si, 1.5 Mn, 0.25 Cr and 0.20 Mo. The Fe content in the coating was determined for a classical galvannealing bath and for a bath according to the invention. Table 1 shows that a significantly higher reactivity is obtained with the Cr-bearing bath according to the invention: the reactivity increases with about 60 %, even thought a significantly lower annealing temperature was used.

Table 1: Annealing reactivity vs. bath composition

Bath (wt.%)	Process	Reactivity (g/m^2 Fe in coating)
0.135 Al; no Cr	20 sec.; 550 °C	4.11
0.135 Al; 0.07 Cr	20 sec.; 530 °C	6.70

As a second example, annealing reactivity data is shown for a classical Ti-IF steel with approximately 0.002 wt.% C, 0.17 wt.% Mn and 0.04 wt.% Ti, the other elements being the normal impurities in steel. The annealing conditions were 30 sec. at 480 °C, which are typical for industrial lines. Figure 1 gives the Fe-content in the coating vs. the Cr-content in the coating bath. It appears that an increase of approximately 3 g/m^2 of Fe is obtained for each 0.10 wt.% Cr added to the bath, both for 0.135 wt.% Al (a conventional galvannealing bath) and for a 0.20 wt.% Al (a conventional galvanising bath). Increased reactivity is demonstrated for the bath with 0.135 Al, allowing faster and/or lower-temperature annealing than without Cr. The effect is already clearly noticed when using 0.02 wt.% Cr. For the bath with 0.20 wt.% Al, the addition of at least 0.05 wt.% Cr is needed (in the annealing conditions of this test) to reach the typical minimum level of 4.5 g/m^2 of Fe in the coating. This Cr-content therefore allows using a galvanising bath with a classical Al-content for galvannealing.